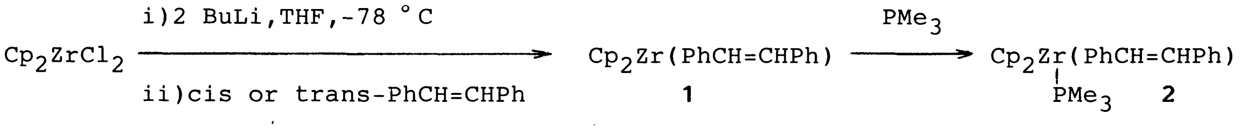
CHEMISTRY LETTERS, pp. 761-764, 1989.

Zirconocene-Alkene Complexes. An X-Ray Structure and a Novel Preparative Method

Tamotsu TAKAHASHI,* Masato MURAKAMI, Masaki KUNISHIGE, Masahiko SABURI,
Yasuzo UCHIDA,* Kozo KOZAWA,† Tokiko UCHIDA,†
Douglas R.SWANSON,†† and Ei-ichi NEGISHI††*
Department of Industrial Chemistry, Faculty of Engineering, The university of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113
†Department of Industrial and Engineering Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278
††Department of Chemistry, Purdue University, W. Lafayette, Indiana 47907, U.S.A.

Structural determination of the first zirconocene-olefin complex, i.e., $Cp_2Zr(PhCH=CHPh)(PMe_3)$, by X-ray crystallography is presented. Zirconium-olefin complexes such as ethylene and butene complexes can be selectively prepared in high yields from dialkylzirconocenes. On treatment of $Cp_2Zr(CH_3)(PhCH_2CH_2)$ with PMe_3, a styrene complex **5** was obtained in good yield.

Zirconocene-alkene complexes have been implicated as intermediates in some zirconium-promoted reactions.[1,2] Recently we have reported the isolation of the first olefin complex, $Cp_2Zr(PhCH=CHPh)(PMe_3)$.[1,3] As reported, treatment of Cp_2ZrCl_2 with 2 equiv. of n-BuLi at -78 °C for 1 h followed by addition of 1 equiv of (E)- or (Z)-stilbene gives the same complex **1** which has been tentatively identified as the trans isomer.[3] However, no definitive structural information has been available. The novel stereoisomerization behavior and its potential mechanistic significance prompted us to unequivocally establish its structure. We report herein the X-ray structure of zirconocene-alkene complex $Cp_2Zr(PhCH=CHPh)(PMe_3)$[4] and a novel selective preparation method for zirconocene-alkene complexes. Although all attempts to isolate **1** as a pure substance have been unsuccessful, addition of one equiv. of PMe_3 to **1** provided $Cp_2Zr(PhCH=CHPh)(PMe_3)$ (**2**) as golden yellow crystals.



$$Cp_2ZrCl_2 \xrightarrow[\text{ii) cis or trans-PhCH=CHPh}]{\text{i) 2 BuLi, THF, -78 °C}} \underset{\mathbf{1}}{Cp_2Zr(PhCH=CHPh)} \xrightarrow{PMe_3} Cp_2\underset{PMe_3}{\underset{|}{Zr}}(PhCH=CHPh)\ \ \mathbf{2}$$

Determination of the structure of **2** by X-ray diffraction analysis yielded the results summarized in Fig. 1. The space group was determined to be $Pbn2_1$ with four molecules in a unit cell of dimensions, a = 13.175(1), b = 21.789(2), c= 8.1395(7) Å. Data collection was carried out by using Rigaku AFC-5 four-circle diffractometer with MoKα (λ = 0.7107 Å) radiation. All possible reflections (3875

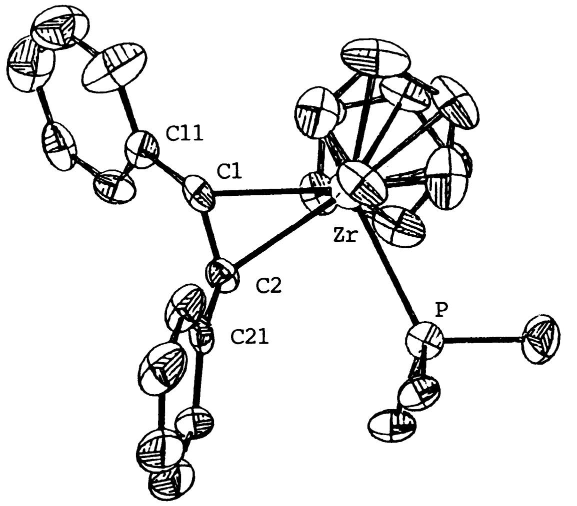


Fig. 1. Molecular structure and atom labeling scheme for **2**.

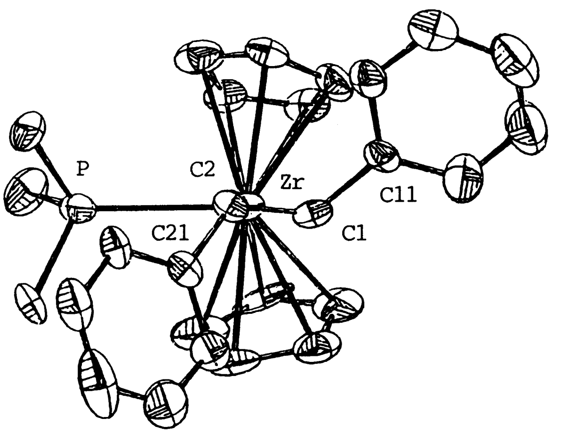


Fig. 2. Sideview of **2**.

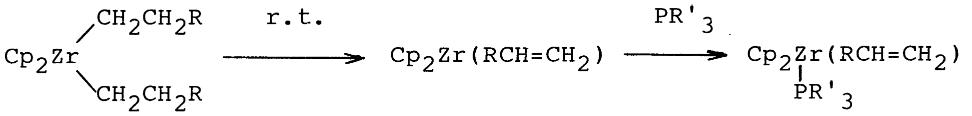
Selected bond lengths(Å) and angles(deg) are as follows: Zr-P = 2.715(5), Zr-C1 = 2.36(2), Zr-C2 = 2.43(2), C1-C2 = 1.38(2), C1-C11 = 1.51(2), C2-C21 = 1.50(2), C1-Zr-C2 = 33.4(5), C11-C1-C2 = 127(1), C21-C2-C1 = 123(1), Zr-C1-C2 = 75.9(9), Zr-C2-C1 = 70.7(9), P-Zr-C1 = 114.5(4), P-Zr-C2 = 81.3(4), Zr-C1-C11 = 123.5(1), Zr-C2-C21 = 125(1).

reflections) in the range $4° < 2\theta < 60°$ were obtained. Of the 3875 reflections collected, 1948 reflections had $|Fo| > 3\sigma(F)$. The structure was refined by the block-diagonal least-squares technique using Rigaku's RASA-5P program and UNICS HBLS-4 for final refinement which resulted in final values of 0.066 and 0.073 for R and Rw, respectively.

The Zr, P, and two carbon atoms C1 and C2 lie in the same plane. The C1-C2 bond distance, 1.38(2) Å, indicates a bond order of approximately 1.7. The C11-C1-C2 and C21-C2-C1 bond angles are 127(1)° and 123(1)°, respectively. The Zr-C1 and Zr-C2 bond lengths of 2.36(2) Å and 2.43(2) Å, respectively, are longer than typical values of the Zr-C bonds, e.g., those in $Zr(CH_2Ph)_4$ (2.27 Å)5) and Cp_2ZrMe_2 (2.27 Å),6) and are comparable to those of Cp_2Zr-diene complexes, e.g., $Cp_2Zr(PhCH{=}CHCH{=}CHPh)$ (2.43 and 2.45 Å)7) and $Cp_2Zr(s\text{-}trans\text{-}CH_2{=}CHCH{=}CH_2)$(2.33 and 2.48 Å).8) Importantly, the trans relationship of the two phenyl group is now firmly established.

The alkene complexes **1** and **2** were prepared by adding stilbene to a zirconocene equivalent which was formed in situ by the reaction of Cp_2ZrCl_2 with 2 equiv. of n-BuLi. In the course of our study we have found that this method has the following critical limitations. (i)The use of π-acidic alkenes such as stilbene are required. (ii)Alkene coupling products are formed in the presence of excess amounts of alkenes. (iii)In some cases 1-butene formed in the reaction mixture reacts with alkenes. For example, zirconocene-styrene complex was obtained in very low yield by this method. Instead, a coupling product with butene was detected.

To overcome these difficulties we have developed a novel selective preparative method for zirconocene-alkene complexes. A typical procedure is as follows. To a mixture of 0.29 g (1 mmol) of Cp_2ZrCl_2 and 5 cm^3 of THF was added 2 cm^3 (1.0 M, 2 mmol) of EtMgBr in THF at -78 °C. The mixture was stirred for 1 h at -78 °C, and Cp_2ZrEt_2 was quantitatively formed in situ. After the addition of 0.14 cm^3 (1 mmol) of PMe_2Ph, the mixture was warmed up to room temperature. Stirring it for 1 h at room temperature led to the formation of $Cp_2Zr(CH_2=CH_2)(PMe_2Ph)$ **3b** in 92% yield. The ^1H-NMR spectra of zirconocene-ethylene complexes **3a-c** revealed notable peaks in the range of 0.0 - 1.0 ppm assignable to the ethylene protons as shown in Fig. 3. Their Cp signals appeared at 4.9 - 5.1 ppm as a doublet. Their ^{13}C- and ^{31}P-NMR spectra were consistent with these formula.[9] Independent of our studies, very recently Alt et al. has reported the X-Ray structure of **3a** obtained from the reaction of $Cp_2Zr(PMe_3)_2$ under high pressure of ethylene gas (50 bar).[10]



$$Cp_2Zr\begin{matrix} CH_2CH_2R \\ CH_2CH_2R \end{matrix} \xrightarrow{r.t.} Cp_2Zr(RCH=CH_2) \xrightarrow{PR'_3} \underset{PR'_3}{Cp_2Zr}(RCH=CH_2)$$

R = H, PR'_3 = PMe_3 **3a**, PMe_2Ph **3b**, $PMePh_2$ **3c**
R = Et, PR'_3 = PMe_3 **4a**, PMe_2Ph **4b**, $PMePh_2$ **4c**

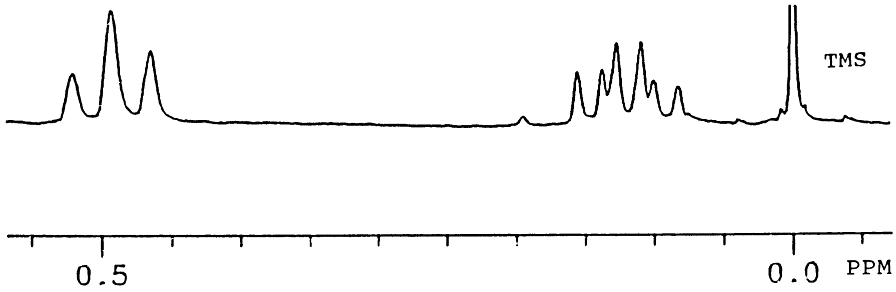


Fig. 3. Notable signals for the ethylene ligand in the ^1H NMR spectrum of **3a**.

When n-BuLi was used, the corresponding zirconocene-1-butene complexes (**4a-c**) were selectively formed in high yields.[11] Interestingly, the use of sec-butyllithium also led to the formation of zirconocene-1-butene complexes. Zirconium styrene complex $Cp_2Zr(PhCH=CH_2)(PMe_3)$ 5[12] was obtained in 70% yield by treatment of $Cp_2Zr(CH_3)(PhCH_2CH_2)$ with PMe_3.[13]

In the case of hafnium, dialkylhafnocene complexes were too stable even at high temperature to give similar olefin complexes. We must await an alternate method for preparing hafnocene-alkene complexes.

We thank Prof. Alt for his information on ethylene-zirconocene before publication. This research was supported by a Grant-in Aid for Scientific Research No.63470078 from the Ministry of Education, Science and Culture (Japan) and the National Science Foundation (CHE-8842237).

References

1) E. Negishi, F. E. Cederbaum, and T. Takahashi, Tetrahedron Lett., 27, 2829 (1986) and references therein.
2) R. F. Jordan, W. E. Dasherand, and S. F. Echols, J. Am. Chem. Soc., 108, 1718 (1986).
3) T. Takahashi, D. R. Swanson, and E. Negishi, Chem. Lett., 1987, 623.
4) The structure of the first zirconocene-alkene complex **2** has recently been

presented. T. Takahashi, Y. Uchida, T. Uchida, and E. Negishi, 13th International Conference on Organometallic Chemistry, Torino, September 1988, Abstr. No.187.

5) G. A. Davies, J. A. J. Jarevis, B. T. Kilbourn, and A. T. Pioli, J. Chem. Soc., Chem. Commun., 1971, 677 and 4511.

6) W. E. Hunter, D. C. Hrncir, R. V. Bynum, R. A. Penttila, and J. L. Atwood, Organometallics, 2, 750 (1983).

7) Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda, and A. Nakamura, J. Chem. Soc., Chem. Commun., 1982, 191.

8) G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, and C. Kruger, J. Am. Chem. Soc., 102, 6344 (1980).

9) **3a:** ^{1}H-NMR(THF-toluene-d_8) δ 0.12(dt, J=7, 11 Hz, 2H), 0.49(t, J=11 Hz, 2H), 1.08(d, J= 6Hz, 9H), 5.08(d, J=2 Hz, 10H); ^{13}C-NMR(THF-toluene-d_8) δ 14.74(d, J=13 Hz), 17.40(d, J=16 Hz), 18.51(d, J=13 Hz), 99.5. ^{31}P-NMR(THF-toluene-d_8) δ 9.04. **3b:** ^{1}H-NMR(THF-toluene-d_8) δ 0.24(dt, J=6, 11 Hz, 2H), 0.68(t, J=11 Hz, 2H), 1.06(d, J=5 Hz, 6H), 4.91(d, J=2 Hz, 10H), 6.9-7.4(m, 5H); ^{13}C-NMR(THF-toluene-d_8) δ 16.43(d, J=20 Hz), 16.89(d, J=12 Hz), 18.45(d, J=4 Hz), 99.89, 128.44, 128.51, 128.94, 130.96, 131.06; ^{31}P-NMR(THF-toluene-d_8) δ 21.95. **3c:** ^{1}H-NMR(THF-toluene-d_8,TMS) δ 0.35(dt, J=6, 11 Hz, 2H), 0.76(t, J=11 Hz, 2H), 1.44(d, J=5 Hz, 3H), 4.96(d, J=2 Hz, 10H), 6.9-7.3(m, 10H); ^{13}C-NMR(THF-toluene-d_8) δ 16.67(d, J=21 Hz), 19.17, 19.25(d, J=11 Hz), 100.37, 128.16, 129.14, 132.70, 132.80; ^{31}P-NMR(THF-toluene-d_8) δ 41.66.

10) H. G. Alt, C. E. Denner, U. Thewalt, and M. D. Rausch. J. Organomet. Chem., 356, C83 (1988).

11) **4a:** ^{1}H-NMR(THF-toluene-d_8) δ -0.29(ddd, J=6, 6, 9 Hz, 1H), 0.44(ddd, J=6, 9, 11 Hz, 1H), 0.84(d, J=6 Hz, 9H), 0.95-1.1(m, 1H), 1.4-1.7(m, 4H), 1.9-2.3(m, 1H), 5.02(d, J=2 Hz, 5H), 5.02(d, J=2 Hz, 5H). ^{13}C-NMR(THF-toluene-d_8) δ 17.18(d, J=16 Hz), 21.00(d, J=12 Hz), 21.35, 35.31, 39.17, 99.65. ^{31}P-NMR(THF-toluene-d_8) δ 39.5. **4b:** ^{1}H-NMR(THF-toluene-d_8) δ -0.19(ddd, J=6, 6, 11 Hz, 1H), 0.47 (ddd, J=6, 9, 11 Hz, 1H), 1.0-1.2(m, 1H), 1.12(d, J=5 Hz, 3H), 1.14(d, J=5 Hz, 6H), 1.3-1.6(m, 3H), 1.9-2.2(m, 2H), 4.95(d, J=1 Hz, 5H), 4.95(d, J=1 Hz, 5H), 6.9-7.4(m, 5H); ^{13}C-NMR(THF-toluene-d_8) δ 16.11(d, J=20 Hz), 16.34(d, J=20 Hz), 21.40, 22.94(d, J=12 Hz), 35.48, 40.56, 100.14, 100.37, 128.43, 128.49, 128.97, 131.00, 131.11; ^{31}P-NMR(THF-toluene-d_8) δ 21.2. **4c:** ^{1}H-NMR(THF-toluene-d_8) δ 0.01 (ddd, J=4, 6, 11 Hz, 1H), 0.69(ddd, J=4, 6, 11 Hz, 1H), 1.0-1.2(m, 1H), 1.3-1.7 (m, 4H), 1.9-2.3(m, 1H), 5.06(d, J=2 Hz, 5H) 5.11(d, J=2 Hz, 5H), 6.9-7.4(m, 10H) ^{13}C-NMR(THF-toluene-d_8) δ 16.46(d,J=21 Hz), 21.36, 25.12(d, J=11 Hz), 35.60, 41.31, 100.42, 100.74, 128.45, 128.63, 128.73, 132.51; ^{31}P-NMR(THF-toluene-d_8) δ 39.5. See also E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. E. Cederbaum, D. R. Swanson and T. Takahashi, J. Am. Chem. Soc., 111, 0000 (1989).

12) **5** (major isomer): ^{1}H-NMR(C_6D_6) δ 0.5-0.9(m, 2H), 0.68(d, J=6 Hz, 9H), 2.74(t, J=11 Hz, 1H), 4.82(d, J=2 Hz, 5H), 5.06(d, J=2 Hz, 5H), 6.90(t, J=8 Hz, 2H), 7.0-7.3(m, 1H), 7.33(t, J=8 Hz, 2H). ^{13}C-NMR(C_6D_6) δ 16.59(d, J=17 Hz), 19.17(d, J=14 Hz), 39.84(d, J=3 Hz), 100.65, 101.93, 119.57, 128.09, 156.16.

13) S. L. Buchwald, and B. T. Watson, J. Am. Chem. Soc., 109, 2544 (1987).

(Received February 10, 1989)